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Non-vacuum method for formation of $CuIn_{0.7}Ga_{0.3}Se_2$ absorber thin film using screen printing and far infrared rapid thermal annealing

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Abstract

Chalcopyrite $CuIn_{0.7}Ga_{0.3}Se_2$ (CIGS) has shown to be as an effective absorber in high-efficiency solar cells. Here, a coating paste containing submicron CIGS powders is screen printed on a glass substrate. The printed wet film is then dried and annealed in a far infrared rapid thermal annealing (RTA) system with and without normal loading. The effects of the RTA temperature and normal loading during annealing on the quality of the CIGS films are evaluated. The carrier concentration and mobility of the film increase when the annealing temperature increases from 400ºC to 600ºC. A three-stage annealing process: 5 min binders/solvents removal at 250ºC, 7 min annealing at 500ºC, and 3 min densification at 600ºC gives a p-type chalcopyrite CIGS film with the carrier concentration in the order of 10^{15} cm^{-3} when a normal loading of 1.97 N cm^{-2} being applied during RTA annealing. There is no carbon being detected in the as-prepared CIGS films after 600ºC densification.

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Keywords: CIGS; Non-vacuum; Screen printing; Far infrared rapid thermal annealing

1. Introduction

$Cu(In_{1-x}Ga_x)Se_2$ (CIGS) with a direct energy band gap showing high absorption coefficient is an ideal absorption material for thin-film solar cells. The conversion efficiency of CIGS solar cell is higher than 20% [1]. The structure of a typical CIGS solar cell involves a front contact, an antireflection layer, a window layer, a buffer layer, a CIGS absorption layer, a back contact and a substrate. CIGS absorption layer is usually prepared by co-evaporation or a two-stage selenization process in a vacuum environment

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[2]. The complex vacuum co-evaporation process causes difficulties in CIGS cell mass productions. Recently, non-vacuum, printing-based processes provide alternative promising routes for CIGS cell mass productions [3]. Suspensions containing CIGS powders are printed on a substrate. CIGS films are then obtained after solvent removal, annealing and densification. This non-vacuum printing approach is compatible with the roll-to-roll coating process and is ideal for low-cost CIGS cell mass production. In this work, $CI_{0.7}G_{0.3}S_2$ films are prepared by screen printing. The wet film was annealed in a far infrared rapid thermal annealing (RTA) system. The effects of the annealing temperature and the normal loading during annealing on the CIGS film qualities are studied.

2. Materials and Method

3.5 g chalcopyrite $CI_{0.7}G_{0.3}S_2$ (CIGS, 99.99%, Materion Advanced Chemicals) particles together with 15 ml anhydrous ethanol (99.8%, Sigma-Aldrich) were ball milled using 20 mm zirconium balls in a 400 rpm planetary ball mill (PM-100, Retsch) for 1 hr. The slurry was dried and further milled using 2 mm zirconium balls with 15 ml anhydrous ethanol in the 400 rpm planetary ball mill for 1 hr. The mean size of the CIGS powders decreased from 105 μm to 0.444 μm after milling (Mastersizer 2000, Malvern). The coating paste containing 3.5 g grinded CIGS powders, 0.5 g ethyl cellulose (UniRegion) and 5 ml α-terpineol (95%, Showa) were homogenized in the 400 rpm planetary ball mill for 1 hr. Coating paste was screen printed on the pre-cleaned glass substrate. The working area was 1 cm x 1 cm. The wet CIGS film was dried in a 100°C oven for 2 min to remove the solvent at the film surface. The film was then in a RTA system with or without normal loading. While in the cases without normal loading, only a 1 g cover glass with the thickness of 1.5 mm was loaded on the CIGS film, a 200 g balance weight was put on top of the cover glass in the normal loading cases. A 200 g weight and a 1 g glass give a normal stress of 1.97N cm^{-2} on the CIGS film during the following annealing program.The CIGS films were annealed in the RTA system (8 x 10^{-3} torr) with the heat rate of 9.5°C/sec using far infrared with a wavelength of 2500 nm - 3000 nm (Ulvac RHL-3610). The annealing program included two/three stages. In the first stage, the film was heated to 250°C and maintained at 250°C for 5 min to remove the solvents. In the second stage, the film temperature increased from 250°C to 400°C or 500°C and maintained at the specific temperature for 7 min to allow the annealing of CIGS powders. Selected CIGS films proceeded the third-stage densification process. The film was densified in RTA at 550°C or 600°C for 3 min. The structure and composition of the annealed films were analyzed by SEM and EDS (JEOL, JSM-5410). The carrier concentration and mobility of film were measured by Hall effect (HMS-3000, USA).

3. Results and Discussion

The film crystallography was tested by XRD and the results indicate that a chalcopyrite $CI_{0.7}G_{0.3}S_2$ film after RTA annealing was obtained. Table 1 shows EDS analysis of the annealed films.

Table 1. EDS analysis of CIGS film after annealing

Weight%	CIGS powder	400°C	500°C	550°C	600°C
C	0	7.41	4.62	3.12	0.92
O	0	2.71	3.17	3.51	1.48
Cu	19.44	18.13	19.16	18.97	19.64
Ga	6.46	6.02	5.94	6.88	6.01
Se	24.77	42.05	42.78	43.41	46.01
In	48.63	23.68	24.33	24.11	25.94

The stoichiometric ratios of CIGS of the annealed films are similar to the original CIGS powders. No CIGS element was removed during RTA annealing. Carbon decreases when increasing the annealing temperature and is nearly not detected after 600°C annealing. The carrier concentration and mobility increase with the increasing of the annealing temperature in Fig 1. CIGS films prepared with a normal loading during annealing show a carrier concentration in the order of 10^{15} cm^{-3} due to its dense structure.

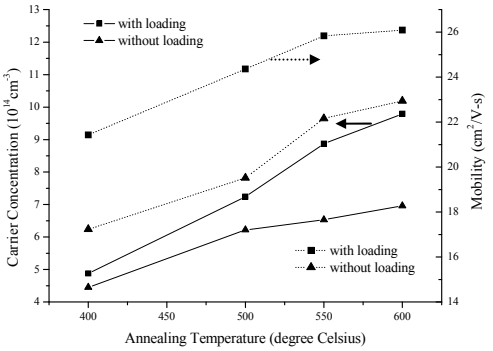

Fig 1. The carrier concentration and mobility of CIGS films

The SEM images of the films annealed at different temperatures without loading and with loading are shown in Figs 2 and 3, respectively. In all cases, the film thickness is around 4 μm. Although the voids between the particles decrease with the increasing of the annealing temperature, distinct boundaries are observed between the CIGS particles when the loading was not applied. When the loading was applied during annealing, the voids between CIGS particles almost disappeared when annealing temperature was greater than 500°C. The film densification due to the normal loading during annealing is achieved.

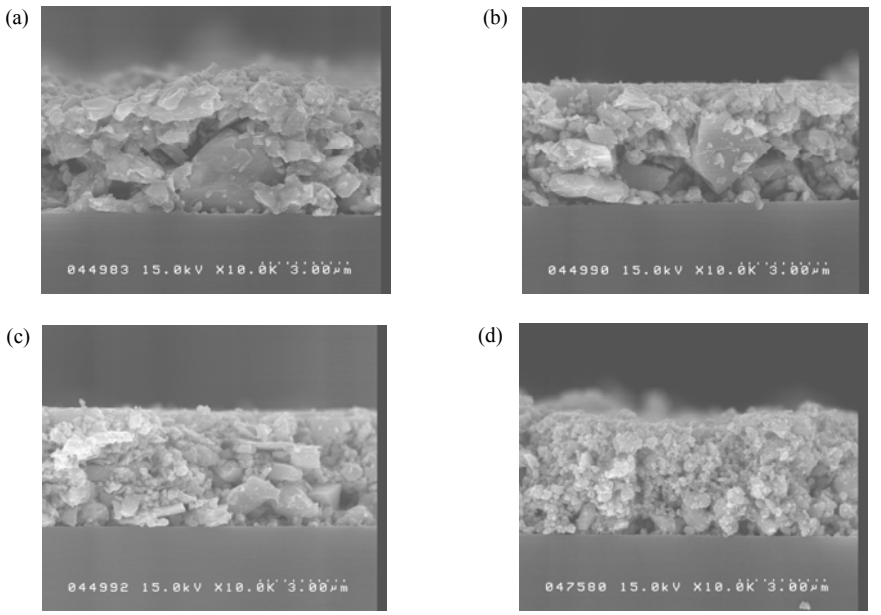

Fig 2. The SEM cross-section micrograph of the annealed CIGS film without normal loading after (a) 400°C, (b), 500°C, (c) 550°C, or (d) 600°C annealing.

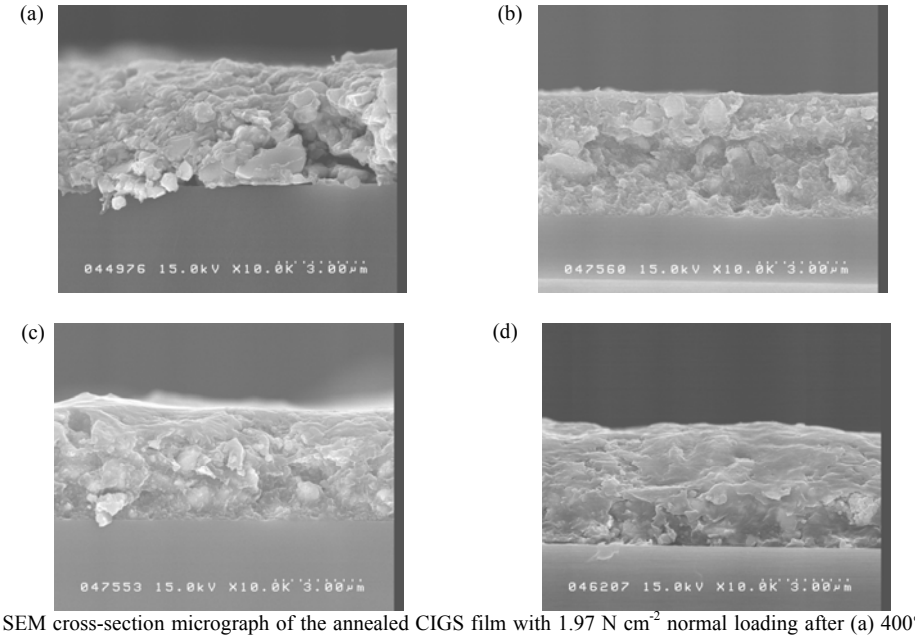

Fig 3. The SEM cross-section micrograph of the annealed CIGS film with 1.97 N cm^{-2} normal loading after (a) 400°C, (b) 500°C, (c)550°C, or (d) 600°C annealing.

4. Conclusion

A non-vacuum method for CIGS film preparation was presented. CIGS films were prepared using screen printing and far infrared RTA annealing. The normal loading during RTA annealing improves CIGS film densification. The solvents were entirely removed after 600°C RTA annealing. A p-type chalcopyrite CIGS film with the carrier concentration in the order of 10^{15} cm^{-3} when a normal loading of 1.97 N cm^{-2} being applied during RTA annealing was successfully prepared.

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Biography

Professor Hsiu-Po Kuo completed his Ph.D. in Chemical Engineering in 2001 at the University of Birmingham, UK. He is the best-contributed editor for Advanced Powder Technology SCI Journal in 2010, 2011 and 2012. His research interests include particle technology, fluidization, renewable energy and coating technology.